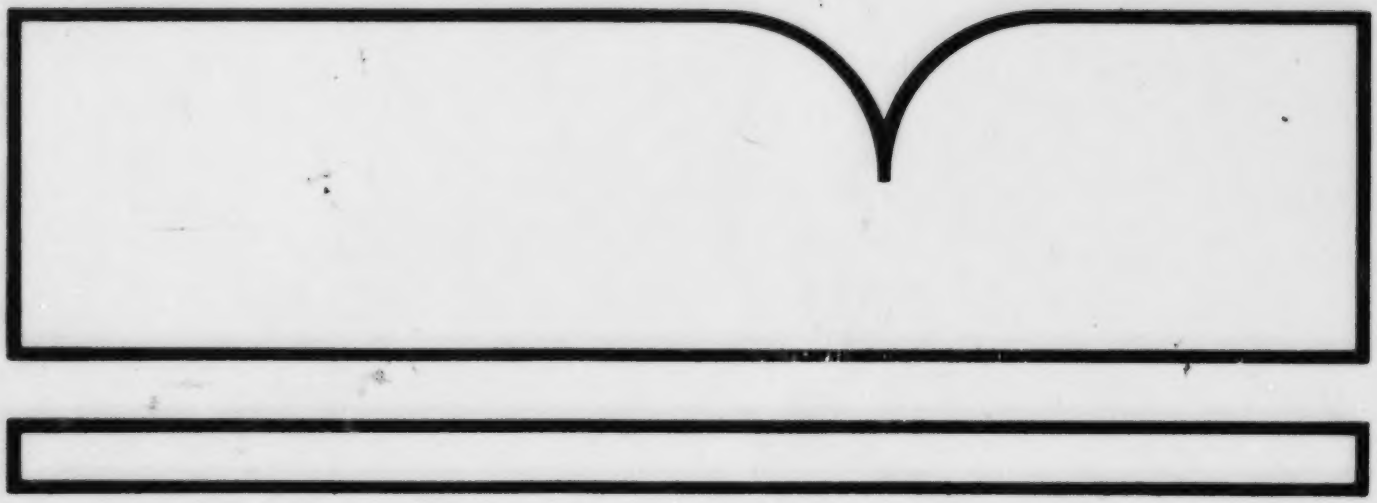
PB82-247560

Accuracy of Pesticide Reference Standard Solutions. Part I. Factors Affecting Organic Solvent Evaporation

(U.S.) Health Effects Research Lab.
Research Triangle Park, NC

4 Aug 81



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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/J-81-090	2. JOURNAL ARTICLE	3. REC PB82-247560
4. TITLE AND SUBTITLE Accuracy of Pesticide Reference Standard Solutions. Par I. Factors Affecting Organic Solvent Evaporation		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) D.W. Hodgson and R.R. Watts		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO. ABZE1A 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Office of Research and Development Health Effects Research Laboratory US Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/11
15. SUPPLEMENTARY NOTES Published in J. Assoc. Off. Anal. Chem., 65(1):89-93, 1982		

16. ABSTRACT

A gravimetric experiment was undertaken to identify the factors affecting solvent evaporation from analytical reference standard solutions and to establish the magnitude of the resultant solvent evaporation. The evaporation of organic solvent from standard solutions is affected by: (1) solvent, (2) container type, (3) solution volume, and (4) storage temperature. Solvents with low vapor pressure-to-surface tension ratios have low evaporation rates. Screw-cap containers with precision-made caps and seals have the lowest evaporation rates. The use of large-volume standard solutions reduces the percent solvent loss, Storage at refrigerator or freezer temperatures can reduce evaporation rate by as much as a factor of 7.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	7
	20. SECURITY CLASS (This page)	22. PRICE

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EPA-600/J-81-090
JOURNAL ARTICLE

pgs. 89-93

REFERENCE STANDARDS

Accuracy of Pesticide Reference Standard Solutions. Part I. Factors Affecting Organic Solvent Evaporation

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A gravimetric experiment was undertaken to identify the factors affecting solvent evaporation from analytical reference standard solutions and to establish the magnitude of the resultant solvent evaporation. The evaporation of organic solvent from standard solutions is affected by: (1) solvent, (2) container type, (3) solution volume, and (4) storage temperature. Solvents with low vapor pressure-to-surface tension ratios have low evaporation rates. Screw-cap containers with precision-made caps and seals have the lowest evaporation rates. The use of large-volume standard solutions reduces the percent solvent loss. Storage at refrigerator or freezer temperatures can reduce evaporation rate by as much as a factor of 7.

The integrity of reference standard solutions should be of primary importance to the analytical chemist. The accuracy of analytical determinations cannot be any better than the accuracy of the reference standard solution used for the analysis.

This laboratory serves as a quality assurance (QA) coordinating center for approximately 30 pesticide residue laboratories. We have often noticed incorrect results from audit sample exercises that could not be traced to laboratory handling error or quantitation technique. For example, results from the analyses of unknown standard solution QA samples are quite often lower than the formulation values. These low results are likely caused by the use of analytical reference standard solutions which have evaporated and therefore concentrated during storage.

A two-part investigation was therefore initiated to gain a better understanding of the various factors affecting the rate of solvent evaporation from the standard solution. This study was intended to identify the magnitude of solvent evaporation under normal laboratory conditions. The experiments were not intended to be a rigorous study of physical chemical properties. The factors studied include choice of solvent, type of container and closure, solution volume, and storage temperature. Part II (1) reports a long-term study of the chemical stability of solutions representing 4 classes of pesticide compounds.

This report has been reviewed by the Health Effects Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.
Received February 4, 1981. Accepted August 4, 1981.

Experimental

Reagents and Equipment

(a) *Solvents.*—Acetone, benzene, ethyl ether (containing 2% ethanol), hexane, isooctane (2,2,4-trimethylpentane), methanol, methylene chloride, and toluene, distilled in glass (Burdick & Jackson Laboratories, Inc.).

(b) *Balance.*—Mettler Model PN163, with plastic dome to reduce air currents.

(c) *Containers.*—(1) Volumetric flasks with glass stoppers, clear glass, 100, 50, 10, and 5 mL.

(2) *Prescription bottles.*—Clear glass with cardboard-lined plastic caps, 3, 1, and ½ oz (Brockway Glass Co., Inc., Brockway, PA), and added Teflon cap liners (A. H. Thomas; No. 2390H).

(3) *Multivials.*—10 mL, clear glass (Supelco, Inc., Bellefonte, PA; No. 3-4579).

(4) *Serum bottles.*—10 mL, with Teflon-lined septa and seals (Wheaton Scientific, Millville, NJ; bottle No. 223739, septum No. 224167, seal No. 224182).

(5) *Small conical vials.*—Clear glass with Teflon-lined caps, or Mininert valves (Supelco, Inc.; 0.3 mL vials No. 3-3291, 0.1 mL vials No. 3-3293, and valves No. 3-3301).

(6) *Small flat-bottom vials.*—Clear glass with Teflon-lined caps, 1.5 and 4 mL (Wheaton Scientific; No. 225170 and 224882).

Experiment Design

The following evaporation rate experiments were performed in duplicate for 10 weeks each:

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(1) hexane and isooctane from an open 10 mL volumetric flask at ambient temperature (without replication, for one day only); (2) 8 solvents from 10 mL glass-stopper volumetric flasks at ambient temperature; (3) hexane from 4 sizes of glass-stopper volumetric flasks (5, 10, 50, and 100 mL) at ambient temperature; (4) hexane from 10 mL glass-stopper volumetric flasks at 3 storage temperatures (ambient, +4°C, and −15°C); (5) hexane and/or isooctane from several types of containers at ambient temperature.

At the beginning of each experiment, the appropriate glassware was weighed empty, filled with test solvent, and weighed again. Volumetric glassware was filled to the mark. Nonvolumetric glassware, such as prescription bottles, was filled to give a head space equivalent to approximately 10% of the container volume. Samples were weighed weekly and returned to storage. Storage temperatures were recorded weekly.

The balance was carefully calibrated against the same 4 reference weights (chosen to be close to the weight of the full containers) before each data collection. To prevent containers from accumulating fingerprint oils, all containers were handled with nylon "lintless" gloves.

Before final data reduction, all data points were corrected for weekly variation by adding the calibration factor from the weighing of the reference weight closest to the weight of the container with solvent. Then all 11 data points (the weight at day zero and each of the 10 weekly weighings) were subtracted from the day zero weight and analyzed by least squares regression of the linear relationship and the linear transforms of the power, exponential, and hyperbolic functions.

The densities 0.664 and 0.689 g/mL were determined for hexane and isooctane, respectively, at ambient laboratory temperature at the beginning of the experiment

Results and Discussion

In all cases, the data analyzed best fit the linear relationship by least squares regression, indicating no change in the rate of solvent evaporation over the 10-week duration of the experiments.

Experiment 1. Evaporation Rates of Solvents from Open Volumetric Flasks

The evaporation rates of hexane and isooctane from an open 10.0 mL volumetric flask at ambient laboratory temperature (24°C) were established without experimental duplication to be 4.7 mL/wk and 1.8 mL/wk, respectively. The evaporation rate of hexane was approximately 3 times that of isooctane under these conditions. The vapor pressure of hexane is 3.0 times that of isooctane at 25°C (2).

Experiment 2. Evaporation Rates of Solvents from Glass-Stopper Volumetric Flasks

The average evaporation rates of hexane and isooctane from duplicate closed 10.0 mL volumetric flasks at ambient temperature (24°C) were established to be 0.15 (±0.07) mL/wk and 0.06 (±0.02) mL/wk, respectively. This difference is significant by Student's *t*-test at the 99% confidence limit. Under these conditions, the hexane evaporation rate is approximately 3 times that of isooctane.

A graph of evaporation rate vs boiling point temperature showed a direct relationship for all test solvents. However, because of the scatter on the plot, it was obvious that boiling point is not the only critical factor. A plot of solvent evaporation rate as a function of the ratio of vapor pressure to surface tension (D. Jernigan, Radian Corp., June 1979) gave a linear correlation coefficient of 0.9827 for the 8 test solvents.

Table 1 lists the experimental values obtained for the evaporation rate and the vapor pressure-to-surface tension ratios (2) of each of the solvents. In addition, there are vapor pressure-to-surface tension ratios listed for other solvents commonly used in the pesticide residue laboratory.

Table 1. Evaporation rates from 10 mL glass-stopper volumetric flasks and vapor pressure/surface tension ratios for some common organic solvents

Solvent	Vapor press./surf. tens. ratio,[a] torr cm/dyne	Evapn rate,[b] mL/wk ± SD
Pentane	33.1	—
Ethyl ether	32.4	0.63 ± 0.17
Methylene chloride	16.0	0.25 ± 0.10
Hexane	8.45	0.15 ± 0.07
Acetone	8.01	0.22 ± 0.01
Chloroform	7.32	—
Methanol	5.65	0.086 ± 0.17
Ethyl acetate	3.97	—
Acetonitrile	3.79	—
Benzene	3.38	0.096 ± 0.0013
Ethanol	2.73	—
Isooctane	2.68	0.058 ± 0.022
Heptane	2.31	—
Isopropanol	2.11	—
Toluene	1.02	0.045 ± 0.0021
Decane	0.04	—

[a] Calculated from Riddick and Burger (2).
[b] Only listed for this work.

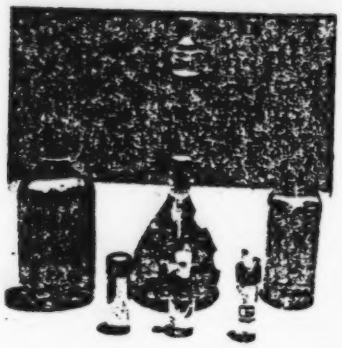

Figure 1. Test containers. Front row (l-r): 4 mL small vial, 0.3 and 1.0 mL conical vials. Back row (l-r): 3 oz prescription bottle, 100 mL volumetric flask, and 25 mL multivial (tested with the glass seal tube removed and closed with the vial cap).

Wrapping Teflon plumber's tape on the outside of the joint between glass stoppers and the neck of the volumetric flask did not reduce the evaporation rate of the solvent inside the container.

Experiment 3. Solution Volume Effects for Glass-Stopper Containers

Four sizes of volumetric flasks were tested in duplicate at ambient temperature to evaluate the effect of solution volume on the solvent evaporation rate. The average evaporation rates of hexane from 5, 10, 50, and 100 mL volumetric flasks were 0.16 (±0.03), 0.15 (±0.07), 0.11 (±0.06), and 0.11 (±0.04) mL/wk, respectively. The decreasing evaporation rates with increasing solution volume in itself makes the larger volume solutions somewhat more desirable. But, more important, the relative evaporation rates (percent of the solution volume evaporated per week) were 3.3, 1.5, 0.23, and 0.10% of the container volume evaporated per week, respectively. Use of larger flasks clearly increases the useful life-time of the reference standards

Experiment 4. Evaporation Rates of Solvents at Different Storage Temperatures

Average evaporation rate for 10.0 mL glass-stopper volumetric flasks filled with hexane and stored in duplicate at ambient temperature (23–24°C), in the refrigerator (+4°C), and in the freezer (−15°C) were 0.15 (±0.07), 0.06 (±0.12), and 0.02 (±0.001) mL/wk, respectively. The rate of loss at refrigerator temperature was approximately a factor of 3 less than rate of loss at ambient. At freezer temperature, the factor was approximately 7 less than ambient. The simple precaution of refrigerator or preferably freezer storage will significantly increase the useful life of standard solutions.

Figure 2. Serum bottle (10 mL) and Teflon-faced septum. Note puncture hole in septum on right after one puncture with standard beveled-point needle from 10 μL Hamilton syringe.

Experiment 5. Evaporation Rates of Solvents from Different Containers

The evaporation rates of isooctane and hexane were determined at ambient temperature for all sizes of glassware listed under *Reagents and Equipment* (Figures 1 and 2).

In Figure 3, the horizontal lines represent the range of the evaporation rates for the solvent/glassware-type combinations. The vertical tick marks on the horizontal lines represent the average evaporation rates calculated for each of the tested sizes of the glassware. In the case of the small vials, the vertical tick marks represent the tested vial size/vial closure combinations used in the experiment.

Volumetric Flasks.—The results in Figure 3 give ample illustration of the fast evaporation rate of hexane and the significantly lower evaporation rate of isooctane from closed volumetric flasks. Care should be taken when closing the flask. A small twist of the stopper greatly improves the seal. When more than 3–5% of the solvent is evaporated, the standard solution should be replaced.

Prescription Bottles.—As seen in Figure 3, the evaporation rates of solvent (both hexane and isooctane) from prescription bottles are somewhat lower than evaporation rates of isooctane from volumetric flasks. The evaporation rate range of the 2 solvents from prescription bottles is 0.01–0.03 mL/wk. These evaporation rates are low enough to keep solvent loss under control from a 50 mL volume. As in the evaporation of solvent from volumetric flasks, firmly tightening

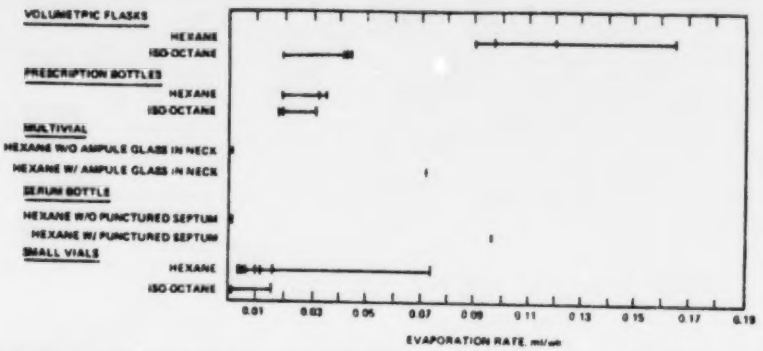

Figure 3. Comparative evaporation rates (mL/wk) of hexane and/or isooctane from different containers at ambient temperature. Range of data for each container is plotted. Vertical lines represent different container volumes (i.e., volumetric flasks and prescription bottles) or different container/cap configurations (i.e., small vials).

the cap on a prescription bottle helps to reduce the solvent evaporation rate. Caps with a hard liner backing underneath the Teflon liner give the best seal. Caps with soft foam-backed seals should be avoided, because they can be totally distorted away from the mouth of the bottle when tightened.

Multivials, Septum Bottles, and Small Vials.—We discourage the use of these containers because of handling problems and/or unacceptable solvent evaporation rates. The solvent evaporation rate from multivials with the ampule top removed, using the container as a screw-cap vial, is almost double the worst case for prescription bottles (0.07 mL/week) unless the glass below the snap-off score line is removed with a punch or pliers. When the glass below the snap-off score line is not removed, protruding sharp edges tear the septum cap seal, resulting in contamination of the solution in the vial. The serum bottle (Figure 2) solvent evaporation rate is almost triple the prescription bottle rate (0.09 mL/wk) *after* the bottle seal has been punctured with the beveled needle of a standard 10 μL Hamilton syringe. The relative evaporation rates from all of the small vials tested (Figure 1) are all greater than 5% of the solution per week, making them useless for long-term storage of standards.

General Considerations

A great deal of caution must be used in the interpretation of the values of the evaporation rates presented in this paper. The evaporation rates presented are a function of within-lot and between-lot container closure variations as well as care taken by the user in firmly sealing the closure. This variability is evident in the low experimental precision in the values reported. Efforts on our part to obtain the same evaporation rates, when the work was performed by another chemist, were unsuccessful. The differences between the evaporation rates of solvents from the various containers proved to be consistent between experimenters, thereby confirming experimental conclusions. Laboratories are also cautioned against applying the same experimental conclusions to similar glassware but of different design or manufacture. The analyst is encouraged to perform his own evaluation of solvent containers which are not specifically covered by this investigation.

Conclusions and Recommendations

The results of this study clearly demonstrate that solvent evaporation from organic reference standard solutions is a significant source of error that must be controlled by the analyst. Solvent evaporation can only be minimized by the proper handling and storage of all organic solutions. From the results of this study and good QA practices, the following general recommendations are made to help minimize solvent evaporation:

(*1*) Use the solvent with the lowest possible evaporation rate or vapor pressure-to-surface tension ratio that will dissolve the material. Isooctane, toluene, and other higher molecular weight hydrocarbons are recommended for the lower polarity pesticides.

(*2*) Choose a container of approximately 100 mL volume, such as prescription bottles or volumetric flasks, for the storage of often-used ref-

erence standard solutions. Alternatively, small volumes may be stored if the solution is divided into several small containers (about 20 mL) and kept in a refrigerator or freezer. They may be withdrawn one at a time, used for a maximum of one week, and then discarded.

(3) Mark the solvent level when the container is originally filled with the solution. Monitor the solvent level in the container. Aliquots of the final dilution (working solution) should not be removed for other uses because then it is impossible to know if solvent has evaporated.

(4) Store solutions that are not in daily use in a refrigerator or freezer to reduce solvent losses.

(5) Seal containers tightly to reduce evaporation from around the cap seal.

(6) If in doubt about solution concentration beyond 3–5%, either check the solution against a solution known to be accurate or replace the standard with a freshly prepared standard.

(7) Do not store standard solutions for more than one year.

Acknowledgments

The authors thank Timothy Holsebach, Vanessa Massenburg, and Regina Smith for their technical assistance.

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